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Optical Nonlinearity of Few-Layer MoS_2 Devices and Applications in Short-Pulse Laser Technology

(Invited Paper)

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***Abstract*—Few-layer transition metal dichalcogenides such as molybdenum disulfide (MoS_2) present new opportunities for photonic devices. Here, we review recent progress in few-layer MoS_2-based nonlinear optics and state-of-the-art pulsed lasers using this new nanomaterial.**

I. Introduction

Low-dimensional nanomaterials hold great promise for photonic devices due to their remarkable optical and electronic properties. Recently, rapid progress has been made with carbon nanotubes (CNTs) and graphene – which are one-dimensional (1D) and two-dimensional (2D) materials respectively – demonstrating that they offer high nonlinearity, ultrafast carrier dynamics and strong saturable absorption, in addition to the potential for large-scale manufacturing techniques which support mass-production of reliable, environmentally-robust devices [1], [2]. However, CNTs and graphene are only a subset of a wider family of nanomaterials, which also include quasi-2D topological insulators (TIs) and few-layer transition metal dichalcogenides (TMDs). Few-layer TMDs, in particular, are experiencing intense research interest for their distinct yet complementary optical properties to CNTs and graphene, which can be engineered by controlling the number of atomic layers [3].

The TMD molybdenum disulfide (MoS_2) has recently been the focus of a significant research effort, building upon a small number of early studies exploring the behavior of thin MoS_2 crystals [4]–[6]. Mono- and few-layer flakes of MoS_2 have been fabricated by numerous different techniques including mechanical exfoliation, solution processing and chemical vapor deposition, and integrated into photonic devices in a variety of ways such as embedding them in polymer composites and deposition on optical components [3], [7] to form saturable absorbers (SAs) for laser short-pulse generation.

II. Nonlinear Optical Properties of Few-Layer MoS_2

While bulk MoS_2 is a semiconductor with an indirect 1.29 eV (961 nm) bandgap, in monolayer form the material exhibits a 1.80 eV (689 nm) direct bandgap [8]. These low-dimensional forms of the material exhibit other favorable optical properties including strong photoluminescence, ultrafast relaxation (<100 fs) and a high third-order nonlinear susceptibility [3], [9]. Such properties suggest ideal behavior as a saturable absorber for short-pulse generation in lasers by mode-locking or Q-switching.

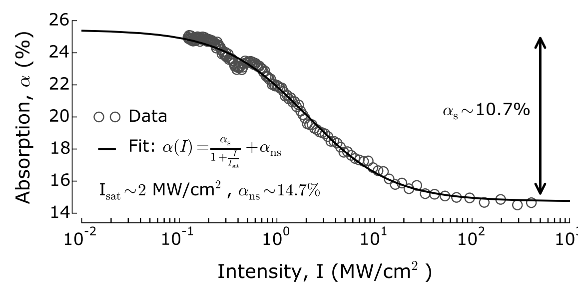

Fig. 1. Nonlinear optical absorption profile of few-layer MoS_2-PVA composite (after [11]), measured by a Z-scan experiment at 1565 nm. Experimental data is fitted with the standard two-level saturable absorber model, to estimate the modulation depth (α_s), saturation intensity (I_{sat}) and nonsaturable loss (α_{ns}) of the device.

We recently reported the fabrication and characterization of 3-5 layer MoS_2 flakes by liquid-phase exfoliation and incorporated MoS_2 flakes into a polyvinyl alcohol (PVA) host to form a free-standing film saturable absorber (described in detail in Refs. [7], [10], [11]). The MoS_2-PVA composite exhibited decreasing absorption with increasing incident light intensity (Fig. 1) in a Z-scan experiment performed at 1565 nm (∼0.80 eV), showing saturable absorption with 10.7% modulation depth and 2.0 MW cm^{-2} saturation intensity. Numerous other studies have fabricated few-layer MoS_2 devices and characterized saturable absorption with modulation depths reported from 1.6% to 35.4% and saturation intensities ranging from 0.43 MW cm^{-2} to 1.85 GW cm^{-2} [7], suggesting that the SA properties can be engineered to suit different applications, for instance by varying the number of layers per MoS_2 flake and changing the longitudinal/lateral flake size [12], [13].

It is perhaps surprising that few-layer MoS_2 can exhibit saturable absorption at infra-red wavelengths, corresponding to photon energies smaller than the expected material bandgap, as the incident photons have insufficient energy to be absorbed. However, this can be explained by defect- and edge-states forming in the bandgap, since few-layer MoS_2 is not an infinite, perfect crystal; thus defects and the high edge to surface area ratio of few-layer flakes enable absorption at sub-bandgap wavelengths [10], [14]. This absorption can be saturated at high intensities by Pauli blocking. Such explanations have

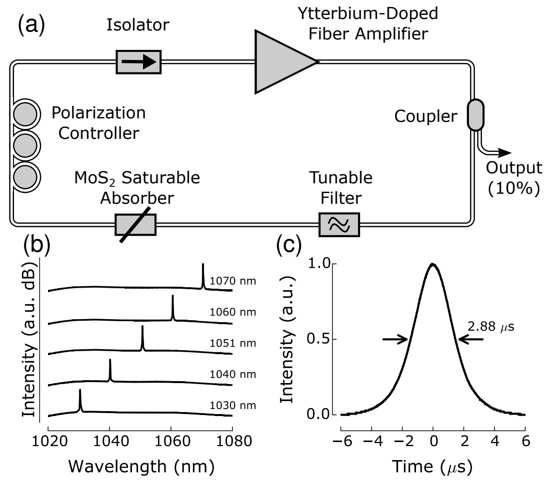

Fig. 2. Q-switched few-layer MoS_2-based fiber laser (after [10]): (a) cavity schematic; (b) spectra within the tunable operating range of 1030-1070 nm; (c) typical Q-switched pulse duration.

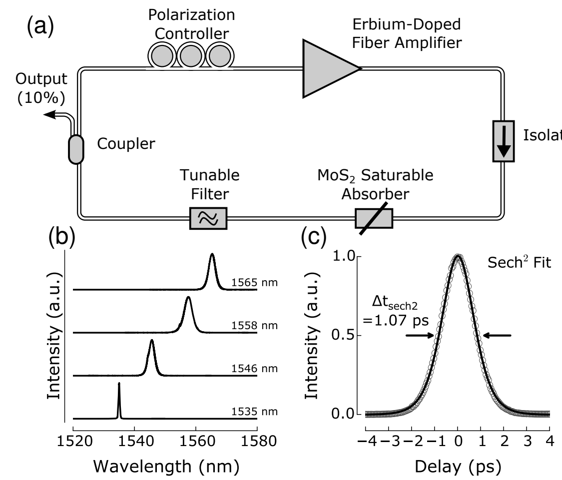

Fig. 3. Mode-locked few-layer MoS_2-based fiber laser (after [11]): (a) cavity schematic; (b) spectra within the tunable operating range of 1535–1565 nm; (c) typical mode-locked pulse autocorrelation trace, well fitted by a $sech^2$ shape.

been supported by defect-state modeling [14] and experimental studies of edge effects [6].

III. MoS_2-based Short-Pulse Lasers

Short-pulse lasers are essential tools for a wide range of applications in materials processing, medicine and research. A saturable absorber acts as a fast passive optical switch, which is included in a laser cavity to produce short-pulses by passive Q-switching or mode-locking. Following measurements of saturable absorption in few-layer MoS_2 devices, MoS_2-based Q-switched bulk [14] and fiber [15] lasers and mode-locked fiber lasers [16] have been reported.

We recently demonstrated a ytterbium-doped fiber laser, tunable from 1030–1070 nm, Q-switched by sandwiching a small (1 mm $\times$ 1 mm) piece of 3-5 layer MoS_2-PVA composite between two fiber ferrules [Fig. 2(a)]. Stable pulses were generated with $\sim$2.88 μs duration at $\sim$74 kHz repetition rate and up to 10.3 mW average output power [Fig. 2(b) & (c)]. Mode-locked operation was also obtained by assembling an erbium-doped fiber laser and including the same few-layer MoS_2-PVA SA device [Fig. 3(a)]. A tunable filter enabled laser operation to be tuned from 1535–1565 nm [Fig. 3(b)] and picosecond pulses at 13 MHz were generated [Fig. 3(c)].

In other literature reports, few-layer MoS_2 SA devices have been demonstrated to mode-lock and Q-switch fiber and bulk lasers within the range 1030 nm to 2100 nm, producing pulses as short as 637 fs and output powers as high as 260 mW. A complete tabulation of all recently reported lasers is presented in Ref. [7].

IV. Outlook

Recent studies have reported numerous novel properties of few-layer MoS_2 which are favorable for photonic technologies. The possibility of using a single SA device for ultrashort pulse generation at a wide range of wavelengths is very promising. Such studies have been complemented by reports of numerous fabrication strategies for obtaining few-layer MoS_2 flakes and integration with different optical components to form flexible SA devices appropriate to the target laser system.

It should be noted that all reported MoS_2-based lasers to date have operated at infra-red wavelengths, corresponding to photon energies lower than the material bandgap. While this can be explained by defect- and edge-state absorption, the direct bandgap of monolayer MoS_2 holds great potential for exploiting MoS_2-based devices in visible lasers at wavelengths coincident with the fundamental bandgap.

Finally, we note that MoS_2 is just one material within a family of layered transition metal dichalcogenides. Other TMDs can be fabricated in few-layer form and have demonstrated novel properties, distinct from their bulk material properties [3]. Such new nanomaterials could offer further opportunities for short-pulse laser development; indeed, tungsten disulfide (WS_2) SAs are starting to emerge: a WS_2 SA was recently reported to mode-lock a fiber laser at 1550 nm [17]. Further work is required to characterize the properties of other TMDs and the applications of MoS_2 beyond short-pulse lasers, although the work to date indicates that these nanomaterials offer new and exciting prospects for future photonic technologies.

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References

[1] P. Avouris, M. Freitag, and V. Perebeinos, "Carbon-nanotube photonics and optoelectronics," *Nature Photon.*, vol. 2, no. 6, pp. 341–350, 2008.

[2] F. Bonaccorso, Z. Sun, T. Hasan, and A. C. Ferrari, "Graphene photonics and optoelectronics," *Nature Photon.*, vol. 4, pp. 611–622, 2010.

[3] Q. H. Wang, K. Kalantar-Zadeh, A. Kis, J. N. Coleman, and M. S. Strano, "Electronics and optoelectronics of two-dimensional transition metal dichalcogenides," *Nat. Nanotechnol.*, vol. 7, no. 11, pp. 699–712, 2012.

[4] R. Frindt and A. Yoffe, "Physical properties of layer structures: optical properties and photoconductivity of thin crystals of molybdenum disulphide," *Proceedings of the Royal Society of London A*, vol. 273, pp. 69–83, 1963.

[5] P. Joensen, R. F. Frindt, and S. R. Morrison, "Single-layer MoS2," *Material Research Bulletin*, vol. 21, pp. 457–461, 1986.

[6] C. B. Roxlo, M. Daage, A. F. Rupper, and R. R. Chianelli, "Optical absorption and catalytic activity of molybdenum sulfide edge surfaces," *J. Catal.*, vol. 100, pp. 176–184, 1986.

[7] R. I. Woodward, R. C. T. Howe, G. Hu, F. Torrisi, M. Zhang, T. Hasan, and E. J. R. Kelleher, "Few-layer MoS2 saturable absorbers for short-pulse laser technology: current status and future perspectives [Invited]," *Photon. Res.*, Doc. ID 231538, In Press, posted 11 Feb. 2015.

[8] K. F. Mak, C. Lee, J. Hone, J. Shan, and T. F. Heinz, "Atomically thin MoS2: a new direct-gap semiconductor," *Phys. Rev. Lett.*, vol. 105, no. 136805, pp. 136 805–1, 2010.

[9] K. Wang, J. Wang, J. Fan, M. Lotya, A. O'Neill, D. Fox, Y. Feng, X. Zhang, B. Jiang, Q. Zhao, H. Zhang, J. N. Coleman, L. Zhang, and W. J. Blau, "Ultrafast saturable absorption of two-dimensional MoS2 nanosheets," *ACS Nano*, vol. 7, no. 10, pp. 9260–9267, 2013.

[10] R. I. Woodward, E. J. R. Kelleher, R. C. T. Howe, G. Hu, F. Torrisi, T. Hasan, S. V. Popov, and J. R. Taylor, "Tunable Q-switched fiber laser based on saturable edge-state absorption in few-layer molybdenum disulfide (MoS_2)," *Opt. Express*, vol. 22, no. 25, p. 31113, 2014.

[11] M. Zhang, R. C. T. Howe, R. I. Woodward, E. J. R. Kelleher, F. Torrisi, G. Hu, S. V. Popov, J. R. Taylor, and T. Hasan, "Solution processed MoS2-PVA composite for sub-bandgap mode-locking of a wideband tunable ultrafast Er:fiber laser," *Nano Res.*, DOI 10.1007/s12274-014-0637-2, In Press, posted 14 Nov. 2014.

[12] K. Wang, Y. Feng, C. Chang, J. Zhan, C. Wang, Q. Zhao, J. N. Coleman, L. Zhang, W. Blau, and J. Wang, "Broadband ultrafast nonlinear absorption and nonlinear refraction of layered molybdenum dichalcogenide semiconductors," *Nanoscale*, vol. 6, p. 10530, 2014.

[13] K.-G. Zhou, M. Zhao, M.-J. Chang, Q. Wang, X.-Z. Wu, Y. Song, and H.-L. Zhang, "Size-dependent nonlinear optical properties of atomically thin transition metal dichalcogenide nanosheets." *Small*, vol. 11, no. 6, p.634, 2015.

[14] S. Wang, H. Yu, H. Zhang, A. Wang, M. Zhao, Y. Chen, L. Mei, and J. Wang, "Broadband few-layer MoS2 saturable absorbers," *Adv. Mater.*, vol. 26, no. 21, pp. 3538–3544, 2014.

[15] R. I. Woodward, E. J. R. Kelleher, T. H. Runcorn, S. V. Popov, F. Torrisi, R. C. T. Howe, and T. Hasan, "Q-switched fiber laser with MoS2 saturable absorber," in Proc. Conf. Lasers Electro-Opt., Jun. 2014, paper SM3H.6.

[16] H. Zhang, S. B. Lu, J. Zheng, J. Du, S. C. Wen, D. Y. Tang, and K. P. Loh, "Molybdenum disulfide (MoS2) as a broadband saturable absorber for ultra-fast photonics," *Opt. Express*, vol. 22, no. 6, pp. 7249–7260, 2014.

[17] K. Wu, X. Zhang, J. Wang, X. Li, and J. Chen, "WS2 as a saturable absorber for ultrafast photonic applications of mode-locked and Q-switched lasers," *arXiv:1411.5777*, posted 21 Nov. 2014.